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| <p>(54) Title: A FINISHING PROCESS FOR HYDROXYL-TERMINATED POLYETHERS</p> <p>(57) Abstract</p> <p>A process for finishing hydroxyl-terminated polyethers containing a Group Ia or IIa metal ion by contacting the polyether with an organic sulphonic acid ester. Mild conditions of the process minimize formation of unwanted byproducts. The process offers the environmental and economic advantage of not having to remove and dispose of products or byproducts. Finished polyethers are well suited to the end applications including their use in the preparation of polyurethane polymers.</p> | | | |

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A FINISHING PROCESS FOR HYDROXYL-TERMINATED POLYETHERS

This invention relates to a finishing process for hydroxyl-terminated polyethers and the reduction of residual basicity therein due to the presence of Periodic Group Ia or IIA 5 metal ions.

Hydroxyl-terminated polyethers are generally prepared by reacting an alkylene oxide with an initiator containing one or more active hydrogen atoms in the presence of a catalyst which usually remains in the polyether. Commonly, the catalysts are basic substances including tertiary amines, or alkali and alkaline earth metal compounds such as, for example, 10 potassium hydroxide or sodium hydroxide. When such polyether is used in the preparation of polyurethane polymer it is found that the residual amounts of basic catalyst interfere with the process of preparing a polyurethane polymer and frequently lead to the formation of poor quality products. Consequently, it is necessary to effect so-called finishing of the "crude" polyether by neutralizing and/or removing the residual catalyst.

15 There are a variety of means of finishing hydroxyl-terminated polyethers. Certain mineral acids are used at various stages of treatment of hydroxyl-terminated polyethers in processes such as those disclosed in U.S. Patents 2,996,550, and 4,507,475; and Japanese Patent J56104936 (J87036052). Water, carbon dioxide and adsorbents such as magnesium silicate are used to remove alkaline catalysts in the process disclosed in U.S. Patent 4,129,718. Water, 20 ortho-phosphoric acid and adsorbents such as magnesium silicate are used to remove alkaline catalysts in the process disclosed in U.S. Patent 4,507,475. In U.S. Patent 3,299,151 the use of formic acid is disclosed. Each of these methods suffers from certain disadvantages, generally in that they involve introducing materials that must later be removed from the polyethers.

The finishing of polyethers can be effected by alternative means which avoid the 25 need to subsequently remove material from the treated polyether by, for example, using ion exchange resins. Japanese Patent J61043629 discloses the finishing of hydroxyl-terminated polyethers with water and certain cationic resins. U.S. Patent 3,271,462 discloses the use of a mercury activated sulfonated polystyrene ion exchange resin for such purpose. However, these methods suffers certain disadvantages in that acidic ion exchange resins, particularly sulfonic 30 acid ion exchange resins, are known to release acids into organic compounds. Acids can be detrimental in certain formulations when forming polyurethanes from the so-treated polyether. Another problem encountered in the use of conventional, acidic, cation exchange resin beds is that the resin is susceptible to deactivation due to fouling. The fouling necessitates recharging of the bed, which is time consuming and decreases output, and the 35 spent resin must be disposed of in an environmentally safe way. A source of fouling can be, for example, propionaldehyde produced by acid hydrolysis of propenyl adducts that may be present in the polyether. Propionaldehyde also imparts an undesirable odor to the polyether,

and if present when preparing a polyurethane foam may cause undesirable discoloration or scorching of the foam.

Thus it would be useful to have a process for the finishing of hydroxyl-terminated polyethers containing alkaline catalysts which would not require subsequent treatment to 5 remove neutralization products or byproducts such as propionaldehyde, incompatible to polyurethane formation, and themselves being waste requiring disposal. It would further be useful if such process employed substances easily handled and not of a corrosive nature such as mineral acids.

The present invention provides a process for finishing crude hydroxyl-terminated 10 polyethers containing Group Ia and Group Ila metal ions without requiring the subsequent removal of metal salts prior to the use of the polyether in end applications such as, for example, the preparation of polyurethane polymer.

In one aspect, this invention is a hydroxyl-terminated polyether composition having an equivalent weight of from 50 to 50000 characterized in that it further comprises:

15 a) from 5 to 5000 ppm of polyether, of a metal sulphonate salt where the metal is from Group Ia or Group Ila of the Periodic Table; and
 b) from 1 to 5000 ppm of polyether, an aliphatic alcohol.

In another aspect, this invention is a process for obtaining a hydroxyl-terminated 20 polyether composition having an equivalent weight of from 50 to 50000 and containing from 5 to 5000 ppm of polyether of a metal sulphonate salt and from 1 to 5000 ppm of polyether of an aliphatic alcohol characterized in that a crude hydroxyl-terminated polyether containing a Group Ia or Ila metal ion is treated with an organic sulphonic acid ester.

Surprisingly, it is found that the sulphonic acid ester treatment of the metal ion in the polyether provides for a finished polyether readily usable in polyurethane applications. 25 The finishing process is a mild, noncorrosive, process and essentially does not result in any unnecessary formation of aldehyde by hydrolysis of unsaturated substances that may be present in the polyether.

The present invention is applicable to a wide range of commonly and conventionally known hydroxyl-terminated polyethers including polyalkylene ethers having at 30 least one hydroxyl group and preferably polyoxyalkylene polyethers having a plurality of hydroxyl groups. As is known to those skilled in the art, such polyethers may be prepared by reacting alkylene oxide(s) with an active hydrogen-containing initiator, typically an alcohol or amine, in the presence of a metal ion of the Periodic Group Ia or Ila or mixtures thereof. If the polyether is to be suitable for end applications the metal ion present in the polyether, and 35 conferring basicity to it, requires treatment to render it neutral. In the invention, such treatment comprises contacting under reaction conditions the polyether with an organic sulphonic acid ester. Sulphonic acid esters are preferred over carboxylic acid esters such as, for example, ethyl acetate, as the metal sulphonate salts formed during the treatment are usually

of better compatibility with the intended end applications. Use of, for example, ethyl acetate would result in a metal acetate content in the polyether which may not be compatible with polyurethane applications.

Suitable organic sulphonic acid esters for use in this invention include those which 5 are preferably liquid at room temperature and are the ester of an aliphatic alcohol with an organic sulphonic acid that can be an aliphatic, but preferably is an aromatic, sulphonic acid. The aliphatic alcohol advantageously is a C₁-6 alcohol such as propanol, butanol, pentanol, or hexanol, and especially methanol or ethanol. The organic sulphonic acid, when an aromatic acid, advantageously includes benzene sulphonic acid, an alkylbenzene sulphonic acid or an 10 alkylnaphthalene sulphonic acid. The alkylbenzene- and alkylnaphthalene sulphonic acids are preferably monoalkyl adducts where advantageously the alkyl radical is a straight chain or branched chain containing from 1 to 12 carbon atoms including, for example, methyl, ethyl, propyl, isopropyl, nonyl, decyl, undecyl or dodecyl moieties. The preferred aromatic sulphonic acids are methylbenzene- and ethylbenzene sulphonic acid. In a highly preferred embodiment 15 of the invention, the sulphonic acid esters employed include the methyl or ethyl ester of methyl or ethylbenzene sulphonic acid with most preferred being the commercially available methyl ester of methylbenzene sulphonic acid.

The amount of ester used is sufficient to substantially or completely treat the free basicity content of the polyether due to the presence of the metal ion. The polyether to be 20 treated may contain the metal ion in an amount up to 5000 ppm of polyether, but usually in from 5 to 1000, more usually in from 5 to 200, and yet more usually from 5 to 100 ppm of polyether. Treatment with the sulphonic acid ester results in the formation of the corresponding metal sulphonate salt and the aliphatic alcohol corresponding to alkyl moiety of the ester. Generally, the ester is present in an amount of from 0.95 to 1.5, preferably from 0.97 25 to 1.2, and more preferably from 0.99 to 1.05 equivalent per equivalent of metal ion to be treated. When the metal ion is in an oxidation state higher than +1, the term "equivalent" is understood to mean equivalent per unity of oxidation; i.e. one mole of a metal 2+ ion will require treatment with $2 \times (0.95 \text{ to } 1.5)$ equivalents of ester. Use of amounts of sulphonic acid ester in excess of this provide a finished hydroxyl-terminated polyether with an 30 unnecessarily high sulphonic acid ester content which on storage could be susceptible to hydrolysis, liberating an acid. An acid content of hydroxyl-terminated polyethers can be disadvantageous in, for example, polyurethane end applications.

To effect treatment of the basicity from the metal ion, the sulphonic acid ester is contacted with the polyether advantageously at a temperature of from 60°C to 150°C, 35 preferably from 80°C to 130°C, and more preferably from 90°C to 125°C typically for a period of from 15 to 600, and preferably from 30 to 300 minutes. At a lower temperature, the time required to treat the metal ion content may be excessively long; while at a higher temperature, detrimental thermal degradation of the polyether may result. The basicity of the polyether can

be monitored by standard acid-base titration techniques to assess the time required to obtain a polyether having little or no free basicity. The actual time required will depend on the metal ion content of the polyether but frequently need not be longer than 60 minutes. The treatment may be effected at ambient pressures but it is found advantageous to conduct the treatment at above ambient pressures in an essentially oxygen-free environment. Such environment can be provided by displacing all air/oxygen as might be present with, for example, nitrogen. Typically the process, will be operated at a pressure of up to 5 bar, but more preferably from 1.5 to 3.5 bars. Exclusion of air/oxygen minimizes any potential oxidation of the polyether while it is being treated with the sulphonic acid ester at the elevated temperature. Further to minimize any potential hydrolysis of the ester during the treatment, the polyether advantageously has a water content of less than 2, preferably less than 1, and more preferably less than 0.8 percent based on total weight of polyether and water.

As already mentioned, the present invention is applicable to treatment of various hydroxyl-terminated polyethers including polyalkylene ethers having at least one hydroxyl group and preferably polyoxyalkylene polyethers having a plurality of hydroxyl groups which are obtained by reacting an alkylene oxide with an initiator in the presence of a substance comprising a Group Ia or IIa metal. Exemplary alkylene oxides suitable for the preparation of polyethers include ethylene oxide, propylene oxide, butylene oxide, amylene oxide, glycidyl ethers such as t-butyl glycidyl ether, phenyl glycidyl ether, styrene oxide and epihalohydrins such as epichlorohydrin, epibromohydrin, 3,3-dichloropropylene oxide, 3-chloro-1,2-epoxypropane, 3-chloro-1,2-epoxybutane and 3,4-dichloro-1,2-epoxybutane. Preferably, the polyethers are prepared from alkylene oxides having from two to four carbon atoms such as ethylene oxide, propylene oxide, and butylene oxide or mixtures thereof.

Illustrative alcohols suitable for initiating formation of a hydroxyl-terminated polyether include polyalcohols such as ethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, 1,5-pentane diol, 1,7-heptane diol, 1,1,1-trimethylolpropane, glycerine, 1,1,1-trimethylethane, hexane-1,2,6-triol, α -methyl glucoside, pentaerythritol, erythritol, sorbitol, glucose, sucrose, fructose or maltose. Also suitable are monoalcohols such as those having from 1 to 18 carbon atoms including methanol, ethanol, isomers of propyl alcohol, isomers of butyl alcohol, and monoalkylethers of diols; and aromatic alcohols such as phenols and compounds derived from phenols such as (4,4'-hydroxyphenyl)2,2-propane, alkylphenols such as dodecylphenol, octylphenol, decylphenol and mixtures thereof.

Illustrative of amines suitable for initiating formation of a hydroxyl-terminated polyether by reaction with alkylene oxide include aliphatic and aromatic mono- and polyamines, optionally having substituents such as alkyl, carboxyl or carboalkoxy groups. Exemplary aromatic amines include aniline, o-chloroaniline, p-phenylene diamine, 1,5-diaminonaphthalene, methylene dianiline, toluene diamine and the condensation products of aniline with formaldehyde. Exemplary aliphatic amines include methylamine,

triisopropanolamine, isopropanolamine, diethanolamine, triethanolamine, ethylenediamine, propylenediamine, butylenediamine, and mixtures of two or more thereof. Amine initiators for polyether adducts are disclosed in, for example, U.S. Patent 4,358,547.

One or more substances catalysts, promoting the reacting of alkylene oxide with 5 initiator are used in the preparation of the hydroxyl-terminated polyether. Conventional catalysts include Periodic Group Ia or Ila alkali or alkaline earth metals or their corresponding hydroxides and alkoxides, Lewis acids, protonic acids or coordination compounds. Preferred catalysts are hydroxides and alkoxides of Group Ia metals including cesium, sodium, potassium, and Group Ila metals including barium or strontium. Potassium hydroxide is more preferred.

10 The resulting polyethers have an average of from 1 to 8 hydroxyl groups per molecule and an equivalent weight ranging from 50 and up to 50000, preferably from 500 to 10000. When the polyether adduct contains from 2 to 8, and preferably from 2 to 4 hydroxyl groups per molecule; the equivalent weight is advantageously from 50 to 5000, preferably from 500 to 4000, and more preferably from 1000 to 3000.

15 In a highly preferred embodiment, this invention pertains to the sulphonic acid ester treatment of a hydroxyl-terminated polyether having a hydroxyl equivalent weight of from 500 to 4000 and being obtained by reacting an initiator containing from 2 to 4 active hydrogen atoms per molecule with an alkylene oxide comprising propylene oxide and optionally ethylene oxide or butylene oxide, in the presence of the metal ion which is sodium, 20 potassium, cesium, barium or strontium. It is found that the use of the sulphonic acid ester is particularly well suited to these polyethers providing for finished products not requiring any subsequent removal of metal salts. The metal alkyl sulphonate salt formed during the finishing process remains in the polyether and is present in an amount commensurate with that of the metal ion. Additionally, the alcohol formed during the finishing process remains in the 25 polyether and is present in an amount commensurate with that of the metal ion. Optionally, if desired, this alcohol content can be reduced by application of reduced pressure.

The hydroxyl-terminated polyethers finished in accordance with disclosed process are characterized as being a composition comprising the hydroxyl-terminated polyether, metal sulphonate salt and an alcohol. The amount of metal sulphonate salt and alcohol present will 30 not exceed the equivalent mole concentration of metal ion which has been treated with the sulphonic acid ester. Typically, the metal salt is present in from 5 to 1000, more typically in from 5 to 200, and yet more typically in from 5 to 100 ppm of polyether; the alcohol being present in similar amounts unless having been reduced in amount by application of reduced pressure. In the latter event, the amount of alcohol present may be as low as 1, and typically is from 1 to 50, 35 preferably from 1 to 20, ppm of polyether. Further, it is found that treatment with sulphonic acid ester essentially avoids hydrolysis of any propenyl unsaturation as might be present. Accordingly, the hydroxyl-terminated polyethers finished in accordance with disclosed process can be further characterized in that they are substantially free of aldehyde such as, for

example, propionaldehyde. By "substantially free", it is understood that the free aldehyde in the hydroxyl-terminated polyether advantageously is less than 10, and preferably less than 5 ppm of polyether.

5 Hydroxyl-terminated polyethers, particularly polyether polyols finished according to the above-described process are eminently suitable for the preparation of polyurethane polymer, and especially flexible polyurethane foam as used for cushioning and upholstery applications.

10 The following examples are given to illustrate the present invention and are not intended to be, nor should they be construed as being, limitative of its scope. All parts and percentages are by weight unless otherwise indicated. Where properties of the polyether are reported these are observed by test procedures including: for pH, ASTM D 1287; water, ASTM E-203; and unsaturation, ASTM D 2849-69. Residual basicity ("CPR") content is determined by acid/base titration using hydrochloric acid.

Example 1

15 A crude glycerine-initiated polyoxyethylene-oxypropylene triol (PO/EO weight ratio 87:13, mixed feed) having a molecular weight of 3000, equivalent weight of 1000, is prepared using conventional methods and using potassium hydroxide to catalyze the alkoxylation reaction. An extraction is conducted to remove potassium hydroxide resulting in a crude polyether containing 100 ppm potassium hydroxide, or alternatively 70 ppm potassium 20 and having a water content of 0.3 wt%.

To the crude polyether at a temperature of 125°C is added, while stirring under a nitrogen atmosphere, toluene sulphonic acid methyl ester (available from Merck, purity 98%) in an amount to provide for a 10 mole percent excess relative to the potassium hydroxide. After maintaining the mixture at these conditions for 3 hours, the treated polyol is cooled to 25 room temperature to provide the finished polyether.

| | <u>Before treatment:</u> | <u>After Treatment:</u> |
|------------------------|--------------------------------|-------------------------|
| pH : | 12 | 8.2 |
| CPR : | 70 | 0.7 |
| Propenyl unsaturation: | 0.009 (meq/g polyether) | 0.009 |
| 30 Propionaldehyde: | < 1ppm (determined by G.C.) | < 1ppm |

35 The residual basicity is reduced to a near zero amount and the polyether now has essentially a neutral pH without loss of unsaturation and the concomitant formation of propionaldehyde.

Comparative Example 2

A sample of the same crude glycerine-initiated polyoxyethylene-oxypropylene triol is treated under equivalent conditions with a 10 mole percent excess of toluene sulphonic

Comparative Example 2

A sample of the same crude glycerine-initiated polyoxyethylene-oxypropylene triol is treated under equivalent conditions with a 10 mole percent excess of toluene sulphonic acid. The resulting polyether is observed to have a pH of 5.5, and a significantly reduced 5 unsaturation content of 0.0005 meq/gram polyol. The propionaldehyde content and CPR has not been determined.

Example 3

Polyurethane Foam is prepared under handmix conditions according to the formulation given below from the polyethers of Example 1 and Comparative Example 2. 10 A similar foam is prepared from an equivalent polyether polyol (Polyether 3) in which the potassium content has been removed by magnesium silicate adsorption.

The results indicate the surprising equivalence of polyurethane foam obtained from Polyether 1 compared to Polyether 3 and superiority to Polyether 2 as can be seen from the observed air flow.

| | <u>parts by weight</u> | <u>Foam 1</u> | <u>Foam 2*</u> | <u>Foam 3*</u> |
|----|--|---------------|----------------|----------------|
| | Polyether of Example 1 | 100 | / | / |
| | Polyether of Example 2* | / | 100 | / |
| 20 | Polyether 3* | / | / | 100 |
| | Water | 2.75 | 2.75 | 2.75 |
| | Tin Octoate | 0.2 | 0.2 | 0.2 |
| | DABCO ^① 33LV | 0.35 | 0.35 | 0.35 |
| | TEGOSTAB ^② B2370 | 0.8 | 0.8 | 0.8 |
| | TDI ^③ 80/20 Index | 105 | 105 | 105 |
| 25 | Blow-off time (sec) | 127 | 119 | 123 119 |
| | Free rise density (kg/m ³) | 34.7 | 36.5 | 34.1 36.5 |
| | Air flow (ft ³ / min) | 3.2 | 2.7 | 3.1 3.2 |

① Amine catalyst - available from Air Products.
 ② Silicon surfactant - available from Th Goldschmidt AG.
 ③ 2,4'- and 2,6'-toluene diisocyanate in a weight ratio of 80:20.
 * Not an example of the invention.

WHAT IS CLAIMED IS:

1. A hydroxyl-terminated polyether composition having an equivalent weight of from 50 to 50000 characterized in that it further comprises:
 - 5 a) from 5 to 5000 ppm of polyether, of a metal sulphonate salt where the metal is from Group Ia or Group Ila of the Periodic Table; and
 - b) from 1 to 5000 ppm of polyether, an aliphatic alcohol.
- 10 2. A process for obtaining a hydroxyl-terminated polyether composition having an equivalent weight of from 50 to 50000 and containing from 5 to 5000 ppm of polyether of a metal sulphonate salt and from 1 to 5000 ppm of polyether of an aliphatic alcohol characterized in that a crude hydroxyl-terminated polyether containing a Group Ia or Ila metal ion is treated with an organic sulphonic acid ester.
- 15 3. A process as claimed in Claim 2 wherein the Group Ia metal ion is sodium, potassium or cesium, and the Group Ila metal ion is barium or strontium.
4. A process as claimed in Claim 3 wherein the metal ion is present in an amount of up to 5000 ppm of polyether and the organic sulphonic acid ester is present in an amount of from 0.95 to 1.5 equivalent per equivalent of metal ion.
- 20 5. A process as claimed in Claim 2 wherein the sulphonic acid ester is an adduct of an aliphatic alcohol with an aromatic sulphonic acid.
6. A process as claimed in Claim 4 wherein the sulphonic acid ester is the methyl ester of methylbenzene sulphonic acid.
- 25 7. A process as claimed in Claim 2 wherein the hydroxyl-terminated polyether is the reaction product of an initiator containing one or more active hydrogen atoms per molecule with an alkylene oxide comprising ethylene oxide, propylene oxide or butylene oxide in the presence of a Group Ia metal ion being sodium, potassium or cesium, or a Group Ila metal ion being barium or strontium.
8. A process for obtaining a finished hydroxyl-terminated polyether of hydroxyl equivalent weight of from 500 to 5000, which has been obtained by reacting an initiator containing from 2 to 8 active hydrogen atoms per molecule with an alkylene oxide comprising ethylene oxide, propylene oxide or butylene oxide, in the presence of a metal ion which is sodium, potassium, cesium, barium or strontium, and which comprises contacting under reaction conditions the polyether containing the metal ion with from 0.95 to 1.5 equivalent, per equivalent of metal ion, of an organic aromatic sulphonic acid ester.
- 30 9. A process as claimed in Claim 8 wherein the the organic sulphonic acid ester is from 0.97 to 1.2 equivalents.
- 35 10. A process as claimed in Claim 9 wherein the organic sulphonic acid ester is the methyl ester of toluene sulphonic acid.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/13312

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/54 C08L71/02 C08G65/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | <p>DATABASE WPI Derwent Publications Ltd., London, GB; AN 76-80091X & JP,A,51 101 099 (SANYO CHEM IND KK) 8 September 1976 see abstract</p> <p>---</p> | 1-10 |
| A | <p>DATABASE WPI Derwent Publications Ltd., London, GB; AN 88-094524(14) & JP,A,63 043 950 (HODOGAYA CHEM IND.) 25 February 1988 see abstract</p> <p>---</p> <p>-/-</p> | 1-10 |

Further documents are listed in the continuation of box C.

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